**Effects of Alkoxide Addition on the Electrochemical Deposition and
Dissolution in Triglyme-based Solution Dissolving Magnesium
Bis(trifluoromethanesulfonyl)amide**

**In-Tae Kim¹, Kazuhiro Yamabuki¹, Masayuki Morita¹, Hiromori Tsutsumi², Nobuko
Yoshimoto^{1,*}**

¹Graduate School of Science and Engineering, Yamaguchi University

2-16-1, Tokiwadai, Ube, 755-8611, Japan

*²Graduate School of Medicine, Yamaguchi University, 2-16-1, Tokiwadai, Ube, 755-8611,
Japan*

*Corresponding author

Phone : +81-836-85-9213

Fax : +81-836-85-9201

Email: nobuko@yamaguchi-u.ac.jp

Abstract

Electrochemical deposition and dissolution of magnesium (Mg) has been examined in triethylene glycol dimethyl ether (triglyme, G3) dissolving magnesium bis(trifluoromethanesulfonyl)amide, $\text{Mg}(\text{TFSA})_2$. The voltammetric current responses at platinum (Pt) electrode in the G3-based electrolytes revealed that the Mg deposition/dissolution process depends on the Mg species in the solution phase. The addition of alkoxides, $\text{Mg}(\text{OC}_n\text{H}_{2n+1})_2$, was effective on the reversibility of the process in $\text{Mg}(\text{TFSA})_2/\text{G3}$. Higher anodic current corresponding to the electrochemical dissolution was observed in the electrolyte solution containing $\text{Mg}(\text{OC}_2\text{H}_5)_2$ as the additive. The morphology of the Mg deposition at the Pt substrate also depended on the additive Mg-alkoxides. The resulting $\text{Mg}(\text{TFSA})_2/\text{G3}$ solutions containing Mg-alkoxides were found to be a possible electrolyte system for rechargeable Mg battery operating at ambient temperature.

Key words: Rechargeable magnesium batteries, magnesium bis(trifluoromethanesulfonyl)amide, triglyme, magnesium alkoxide

1. Introduction

Rechargeable magnesium (Mg) battery has widely attracted much attention as a possible candidate of so-called next generation batteries because of the merits on high volumetric capacity (3832 Ah L^{-1}), high specific capacity (2230 Ah kg^{-1}), low electrode potential (-2.356 V vs. SHE) of Mg metal as the negative electrode, and natural abundance of Mg resources. One of the key issues to realize a practical rechargeable Mg battery system is the sufficient rechargeability of Mg negative electrode in non-aqueous electrolyte systems. Unlike lithium (Li), Mg does not show good reversibility in non-aqueous electrolyte solutions dissolving such conventional Mg salts as MgCl_2 , $\text{Mg}(\text{ClO}_4)_2$ and $\text{Mg}(\text{CF}_3\text{SO}_3)_2$, due to the formation of passivating layers on Mg surface [1-3].

Up to the present, it has been considered that the promising electrolyte systems should consist of tetrahydrofuran (THF) as solvent and organo-metal complexes as Mg sources for rechargeable Mg electrode [3-6]. The THF-based solution shows excellent cyclability, but THF has some drawbacks such as narrow electrochemical window (less electrochemical stability), corrosive nature to metal substrate and high volatility, and therefore, alternative organic solvents are still required to construct more stable and reliable electrolyte systems for rechargeable Mg batteries.

Recently, oligo(ethylene glycol) dimethyl ethers, so called glyme family, have been proposed for Li-ion battery system. In general, glymes consisting of oligo(ethylene oxide) units, $-(\text{CH}_2\text{CH}_2\text{O})_n-$, can interact with alkali metal cations of Li^+ , Na^+ etc. to form complexes in solution phases [7]. Watanabe et al. have reported the chemical structures of the complexes of Li salt in tetraglyme (G4) and pentaglyme (G5) by X-ray analysis and Raman spectroscopy [8]. They also proved that the glyme-based complexes can serve as liquid electrolytes in Li-battery system [7]. Since these glymes show higher boiling points and lower vapor pressure than THF, they are also attractive solvents for Mg batteries.

We have examined Mg salt-containing electrolytes with lower vapor pressure for rechargeable Mg electrode. Ionic liquid-based electrolyte, $\text{Mg}(\text{TFSA})_2$ dissolved in EMITFSA (EMI: 1-ethyl-3-methylimidazolium, TFSA: bis(trifluoromethanesulfonyl)amide), and polymeric gel electrolyte containing $\text{Mg}(\text{TFSA})_2$ showed satisfactory high ionic

conductivity and good thermal and electrochemical stability [9-12]. On the other hand, Abe et al. have investigated the Mg electrode behavior in 2-methyltetrahydrofuran dissolving MgBr_2 electrolyte ($\text{MgBr}_2/2\text{-MeTHF}$) [13, 14]. They found that the addition of Mg-ethoxide, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, shows a drastic increase in the coulombic efficiency for Mg deposition and dissolution at elevated temperature at room temperature.

In the present work, we have examined an electrolyte system of $\text{Mg}(\text{TFSA})_2$ dissolved in triglyme (G3: $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$) whose vapor pressure is much lower than those of THF families. The effects of Mg-alkoxides ($\text{Mg}(\text{OC}_n\text{H}_{2n+1})_2$) addition were investigated for electrochemical deposition and dissolution of Mg in $\text{Mg}(\text{TFSA})_2/\text{G3}$. We used methoxide, $\text{Mg}(\text{OCH}_3)_2$, and ethoxide, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, as the additive components, and focused on the changes in the voltammetric responses for Mg deposition/dissolution from/to the solutions with and without the additives. Influences of the additives on the morphology of the deposit were also investigated under ambient temperature conditions.

2. Experimental

2.1. Preparation of the electrolyte solution

High purity $\text{Mg}(\text{TFSA})_2$ (< 99.9 %, Morita chemical) was used as the electrolyte salt for Mg deposition/dissolution, which was dried under a vacuum at 120 °C for 48 h and stored in a glove box filled with dry Ar (the dew point < -90 °C) at ambient temperature. The glyme G3 (Alfa Aesar, 99.0 %) was treated to remove dissolved oxygen and water by molecular sieves, until the residual water contents in the solvents to be less than 100 ppm. The Mg salt was dissolved in G3 solvent to make 0.7 mol dm⁻³ (M) solution, $\text{Mg}(\text{TFSA})_2/\text{G3}$. The alkoxides, $\text{Mg}(\text{OCH}_3)_2$ and $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (< 99.3%, Kojundo Chemical), were used as-received for the electrolyte additives. For comparison, solutions using G3 solvent without $\text{Mg}(\text{TFSA})_2$ were also examined, in which DEMETFSA (Kanto Chemical, DEME: *N, N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium) was used as the supporting electrolyte.

2.2. Electrochemical measurements

The ionic conductivities of electrolyte solutions were measured by ac impedance method (10⁵ Hz ~ 10 Hz, 10 mV_{p-p}) using a frequency response analyzer with electrochemical

measurement equipment (Hokuto denko, HZ-7000). The electrochemical deposition and dissolution processes of Mg in the electrolyte solution were investigated by cyclic voltammetry (CV) using a potentiostat/galvanostat (Bio-logic science instrument, VSP-300) at ambient temperature (298 ± 3 K). A conventional 3-electrode beaker cell was using a Pt sheet (0.5 cm^2) as the working electrode, and the quasi-reference and counter electrode were using Mg rod and Pt sheet with a large surface area (3.0 cm^2), respectively. The potential scanning range and rate in CV were -2.0 to 2.0 V (vs. Mg) and 20 mV s^{-1} , respectively.

A cathodic deposition of Mg was also conducted under a potentiostatic condition at -2.0 V vs. Mg/Mg^{2+} for 10 min. The resulting deposit was characterized by X-ray diffraction and scanning electron microscopy (SEM) observation (Keyence, VE-8800).

3. Results and Discussion

3.1. Electrochemical behavior of the additives

The temperature dependence of the ionic conductivities in $\text{Mg}(\text{TFSA})_2/\text{G3}$ electrolyte with or without Mg-alkoxides measured by the ac impedance method is shown in Fig. 1. The ionic conductivity of $\text{Mg}(\text{TFSA})_2/\text{G3}$ is not significantly changed by the addition of Mg-alkoxides.

In order to understand basic electrochemical behavior of the Mg-alkoxides, CV experiments was carried out using the G3-based solutions without $\text{Mg}(\text{TFSA})_2$. Figure 2 shows CV responses of Pt electrode in the G3 solutions dissolving (a) $0.35 \text{ M Mg}(\text{OCH}_3)_2$, (b) 0.1 M DEMETFSA , (c) $0.1 \text{ M DEMETFSA} + 0.35 \text{ M Mg}(\text{OCH}_3)_2$ and (d) $0.7 \text{ M Mg}(\text{TFSA})_2$. In the solution of $0.7 \text{ M Mg}(\text{TFSA})_2/\text{G3}$, the cathodic current increase at -0.5 V or below and the anodic current peak at $+1.5$ V were observed, which would mainly correspond to the electrochemical deposition and dissolution of Mg, respectively. Despite of lower ratio in the anodic current to the cathodic one, the CV response in $\text{Mg}(\text{TFSA})_2/\text{G3}$ strongly suggests that the electrochemical deposition and dissolution of Mg should occur on Pt electrode in this electrolyte system at ambient temperature. Similar results have been recently reported by Oriksa et al. [15], in which the process was shown at higher temperature (373K) with rather high overpotential. By comparing the current responses of curves a and c in Fig. 2, the cathodic deposition and anodic dissolution of Mg can proceed in $\text{DEMETFSA}/\text{G3}$ containing

Mg(OCH₃)₂. Much lower current response observed in Mg(OCH₃)₂/G3 would indicate that sufficient concentration of ionic species is required for the deposition/dissolution processes. We observed significant difference in the onset potentials for Mg deposition and dissolution (the potentials where the anodic and cathodic currents respectively increase) between curves c and d. Differences in the electrolyte properties, such as ionic species, ionic strength and conductivity, are probably responsible for these differences although their details are still unknown at the present stage.

3.2. Influences of the additives in the electrolyte solution

Figure 3 shows the cyclic voltammograms of Pt in the Mg(TFSA)₂/G3 solution with Mg-alkoxides additives. Here, the molar ratio of the additives to Mg(TFSA)₂ was 1:5 (the absolute molar concentration of the additives was 0.14 M). The anodic current was slightly increased with the addition of Mg-methoxide, Mg(OCH₃)₂. When Mg-ethoxide, Mg(OC₂H₅)₂, was added, both the cathodic and anodic currents increased significantly. The onset potentials for both cathodic deposition and the anodic dissolution shifted to the direction of lower overpotential. These results prove that the alkoxide in the solution can enhance the electrochemical Mg deposition/dissolution processes in Mg(TFSA)₂/G3. Also, smaller anodic current peak or shoulder was observed at around 0.3 V in the solutions containing the alkoxides, which would correspond to the current response in DEMETFSA+Mg(OCH₃)₂/G3, shown in Fig. 2d. These CV responses suggest that the anodic process consists of at least two steps in the Mg(TFSA)₂/G3 system containing alkoxides.

Influences of the Mg alkoxides on the morphology of Mg deposition were investigated by SEM observation. The cathodic deposition of Mg was carried out on Pt sheet substrate at constant potential (-2.0 V vs. Mg/Mg²⁺) for 10 min in 0.7 M Mg(TFSA)₂/G3 with or without the additives. Figure 4 shows SEM images for the deposits obtained from the electrolyte (a) without additives and (b) with 0.14 M Mg(OCH₃)₂. It was confirmed that the both deposits are Mg metal with hexagonal crystalline by XRD measurements. The SEM images also reveal that the deposits consist of spherical particles with micrometer-order sizes. From the solution without additives, the deposit tends to form rather smooth surface spheres (Fig. 4a). This observation is consistent with that recently reported by other research groups using similar

glyme-based electrolytes [15, 16]. On the other hand, the deposition from the electrolyte containing $\text{Mg}(\text{OCH}_3)_2$ gave aggregation of smaller sizes of sphere and flake (Fig. 4b). The difference in the current response for anodic dissolution given in Fig. 3 would reflect such differences in the surface morphology of the deposit as shown in Fig. 4. Thus, the addition of alkoxides would control the morphology of the Mg deposition, and hence affect the rate of anodic dissolution in the glyme-based electrolyte solution, although details of the actual mechanism of the additive's function are still unclear. Variations in the ionic structure and physicochemical properties that could influence the electrochemistry of Mg in glyme-based electrolyte systems are now under investigation.

4. Conclusion

We have investigated the electrochemical deposition and dissolution of Mg in triglyme (G3) containing $\text{Mg}(\text{TFSA})_2$ with alkoxides, $\text{Mg}(\text{OC}_n\text{H}_{2n+1})_2$, as the additive components. The process in the $\text{Mg}(\text{TFSA})_2/\text{G3}$ system was enhanced significantly by the alkoxide addition even at ambient temperature (around 298 K). Changes in the surface morphology of the deposit would lead to the shift of the onset potential (decrease in the overpotentials) for both the cathodic deposition and anodic dissolution. The resulting $\text{Mg}(\text{TFSA})_2/\text{G3}$ containing $\text{Mg}(\text{OC}_n\text{H}_{2n+1})_2$ additives can be used as an electrolyte system that works for reversible Mg metal electrode at ambient temperature.

Acknowledgments

This work was partly supported by the Advanced Low Carbon Technology Research and Development Program (ALCA, Contract No. 11102784) from Japan Science and Technology Agency (JST).

References

- [1] T. D. Gregory, R. J. Hoffman, R. C. Wintertem, *J. Electrochem. Soc.*, 1990, 137, 775-780.
- [2] P. Saha, M. K. Datta, O. I. Velikokhatnyi, A. Manivannan, D. Alman, P. N. Kurnta, *Prog. Mater. Sci.*, 2014, 66, 1-86.

- [3] Z. Lu, A. Schechter, M. Moshkovich, D. Aurbach, *J. Electroanal. Chem.* 1999, 466, 203-217.
- [4] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, *Nature*, 2000, 407, 724-727.
- [5] D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer, I. Goldberg, *J. Electrochem. Soc.*, 2002, 149(2), A115-A121.
- [6] Y. Viestfrid, M.D. Levi, Y. Gofer, D. Aurbach, *J. Electroanal. Chem.*, 2005, 576, 183.
- [7] K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, *J. Electrochem. Soc.*, 2012, 159(7), A1005-A1012.
- [8] T. Mandai, R. Nozawa, S. Tsuzuki, K. Yoshida, K. Ueno, K. Dokko, M. Watanabe, *J. Phys. Chem. B*, 2013, 117, 15072-15085.
- [9] N. Yoshimoto, Y. Tomonaga, M. Ishikawa, M. Morita, *Electrochim. Acta*, 2001, 46, 1195-1200.
- [10] N. Yoshimoto, S. Yakushiji, M. Ishikawa, M. Morita, *Electrochim. Acta*, 2003, 48, 2317-2322.
- [11] N. Yoshimoto, M. Matsumoto, M. Egashira, M. Mortia, *J. Power Sources* 195 (2010) 2096-2098.
- [12] T. Kakibe, N. Yoshimoto, M. Egashira, M. Mortia, *Electrochem. Commun.* 12 (2010) 1630-1633.
- [13] K. Asaka, K. Miyazaki, T. Fukutsuka, T. Abe, K. Nishio, Y. Uchimoto, *PRiME 2012 abstract* (2012).
- [14] T. Abe, K. Miyazaki, T. Fukutsuka, K. Nishio, Y. Uchimoto, 224th ECS meeting abstract (2013).
- [15] Y. Orikasa, T. Masese, Y. Koyama, T. Mori, M. Hattori, K. Yamamoto, T. Okado, Z.-D. Huang, T. Minato, C. Tassel, J. Kim, Y. Kobayashi, T. Abe, H. Kageyama, Y. Uchimoto, *Sci. Reports*, 2014, 4, 5622-5627.
- [16] S.-Y. Ha, Y.-W. Lee, S. W. Woo, B. Koo, J.-S. Kim, J. Cho, K. T. Lee, N.-S. Choi, *Appl. Mater. Interfaces*, 2014, 6, 4063-4073.

Figure captions

Fig. 1 Temperature dependence of ionic conductivities of G3 solutions containing (■) 0.7 M $\text{Mg}(\text{TFSA})_2$, (○) 0.7 M $\text{Mg}(\text{TFSA})_2$ + 0.14 M $\text{Mg}(\text{OCH}_3)_2$ and (▲) 0.7 M $\text{Mg}(\text{TFSA})_2$ + 0.14 M $\text{Mg}(\text{OC}_2\text{H}_5)_2$.

Fig. 2 Cyclic voltammograms of Pt electrode in G3 solutions containing (a) 0.35 M $\text{Mg}(\text{OCH}_3)_2$, (b) 0.1 M DEMETFSA, (c) 0.1 M DEMETFSA + 0.35 M $\text{Mg}(\text{OCH}_3)_2$ and (d) 0.7 M $\text{Mg}(\text{TFSA})_2$.

Fig. 3 Cyclic voltammograms of Pt electrode in G3 solutions containing (a) 0.7 M $\text{Mg}(\text{TFSA})_2$, (b) 0.7 M $\text{Mg}(\text{TFSA})_2$ + 0.14 M $\text{Mg}(\text{OCH}_3)_2$ and (c) 0.7 M $\text{Mg}(\text{TFSA})_2$ + 0.14 M $\text{Mg}(\text{OC}_2\text{H}_5)_2$.

Fig. 4 SEM images of Mg deposited on Pt substrate electrode after cathodic deposition at -2.0 V (vs. Mg/Mg^{2+}) for 10 min in (a) 0.7 M $\text{Mg}(\text{TFSA})_2/\text{G3}$ and (b) 0.7 M $\text{Mg}(\text{TFSA})_2$ + 0.14 M $\text{Mg}(\text{OCH}_3)_2/\text{G3}$.

Fig. 1 (Kim, et al.)

Fig. 2 (Kim, et al.)

Fig. 3 (Kim, et al.)

Fig. 4 (Kim, et al.)